Dynamic Simulation of Adiabatic Catalytic Fixed-Bed Tubular Reactors: A Simple Approximate Modeling Approach

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Fixed-bed tubular reactors are used widely in chemical process industries, for example, selective hydrogenation of acetylene to ethylene in a naphtha cracking plant. A dynamic model is required when the effect of large fluctuations with time in influent stream (temperature, pressure, flow rate, and/or composition) on the reactor performance is to be investigated or automatically controlled. To predict approximate dynamic behavior of adiabatic selective acetylene hydrogenation reactors, we proposed a simple 1-dimensional model based on residence time distribution (RTD) effect to represent the cases of plug flow without/with axial dispersion. By modeling the nonideal flow regimes as a number of CSTRs (completely stirred tank reactors) in series to give not only equivalent RTD effect but also theoretically the same dynamic behavior in the case of isothermal first-order reactions, the obtained simple dynamic model consists of a set of nonlinear ODEs (ordinary differential equations), which can simultaneously be integrated using Excel VBA (Visual BASIC Applications) and 4th-order Runge-Kutta algorithm. The effects of reactor inlet temperature, axial dispersion, and flow rate deviation on the dynamic behavior of the system were investigated. In addition, comparison of the simulated effects of flow rate deviation was made between two industrial-size reactors.

Keywords: Dynamic simulation, 1-D model, Adiabatic reactor, Acetylene hydrogenation, Fixed-bed reactor, Axial dispersion effect

INTRODUCTION

The cracking of naphtha feedstock produces a stream composed of mainly ethylene, some paraffins, diolefins, aromatics, and minute amount of acetylene. Ethylene is mainly used in the production of polymers, especially...
polyethylene (PE). However, small amounts of acetylene, on the order of parts per million, are harmful to the catalysts used in polymerization (Schbib et al. 1996). Therefore, acetylene in the ethylene stream must be selectively hydrogenated with a minimum loss of ethylene. In the petrochemical industry there are two different routes for this ethylene purification: tail-end and front-end hydrogenation (Schbib et al. 1994). The most effective method for removing acetylene, down to 2-3 ppm, is selective hydrogenation over palladium catalysts in a multi-bed adiabatic reactor. The objective of this work is to develop a high-speed dynamic adiabatic 1-D model with/without axial dispersion for an industrial reactor of a tail-end acetylene hydrogenation system.

It has been reported that, at the end of a reactor run (shutdown for decoking) which is the worst condition, the maximum pressure drop across the reactor’s bed length is about 0.2 bar, which is less than 1% of its operating pressure (about 35 bar) (Gobbo et al. 2004). This behavior is consistent with our plant data. Therefore, any change in reactor pressure may be considered insignificant and momentum balance can be omitted from our model. Gobbo et al. (2004) also reported that, at the exit of the first reactor, the largest temperature difference between the central point (r = 0) and peripheral point (r = R) was just 4.9 K. Therefore, radial temperature gradient needs not be considered in our model. Our preliminary investigation and simulation results show that, when commercial 100~200 micrometer thick egg-shell type Pd/alumina catalyst is used, the retarding effect of intraparticle diffusion inside the catalyst pellet (3-4 mm in diameter) on the reaction rate is negligible and the effectiveness factor can be taken as essentially unity. The developed model aims to satisfactorily predict the outlet values and provide reasonable axial profiles of temperature and concentrations of acetylene, hydrogen, ethylene, and ethane in the reactor as functions of time. The effect of plug-flow with/without axial dispersion, as reflected by the change in residence time distribution (RTD) is accounted for in the model by a specific number of CSTR compartments connected in series. The effects of reactor inlet temperature, axial dispersion, and flow rate deviation on the dynamic behavior of the system will be investigated. In addition, comparison of the simulated effects of flow rate deviation will be made between two reactors of industrial scale.

Dynamic Model of Tubular Fixed-Bed Reactor

The unsteady-state multi-component mass and energy balance equations for a tubular fixed-bed reactor with only axial dispersion are derived as:

\[
\frac{\partial c_\alpha}{\partial t} + \frac{\partial}{\partial z} (c_\alpha v_z) = D_{\text{eff},\alpha} \left( \frac{\partial^2 c_\alpha}{\partial x^2} \right) + c \frac{\partial^2 X_\alpha}{\partial z^2} + \frac{\rho_p(1 - \varepsilon)}{\varepsilon} \sum_{k=1}^{m} (\Delta H_{R,k} \eta_k)
\]

\[
c^2 \frac{\partial T}{\partial t} + \frac{\partial}{\partial z} (\varepsilon T v_z) = -\frac{\rho_p(1 - \varepsilon)}{\varepsilon} \sum_{k=1}^{m} (\Delta H_{R,k} \eta_k)
\]

In the case of plug flow, the effective dispersion coefficient \( D_{\text{eff},\alpha} \) becomes zero and the first term on the right-hand side of (1) will disappear. In principle, the above
coupled partial differential equations may be integrated numerically together with the appropriate kinetic rate expressions, and applicable initial and boundary conditions to obtain the system’s dynamic behavior. Though various powerful sophisticated commercial software packages are available, the required computational time on a typical notebook PC is generally substantial. In addition, oftentimes the numerical integration or solution might run into numerical instability issue or fail to converge correctly. As an alternative, we have proposed and developed an approximate numerical approach which is not only fast but also makes use of widely available Microsoft Excel.

**DERIVATION OF 1-DIMENSIONAL DYNAMIC MODEL**

CSTR and plug-flow reactor (PFR) assume ideal flows with instantaneous complete mixing and piston movement, respectively. Generally, elements of fluid taking different routes through a reactor may require different lengths of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the vessel is called the residence time distribution (RTD) of the fluid. The RTD curve is needed to account for nonideal flow behavior, including axial dispersion effect in a plug-flow reactor (Levenspiel 1972). In theory, the RTD of a PFR can be obtained from the equivalent case of $N$ tanks of CSTR connected in series, as $N$ approaches infinity while the individual tank volumes approach zero and the total tank volume remains the same as that of the PFR. Similarly, the RTD of a PFR with axial dispersion of fluid can be approximated by a suitable finite number $N$ of CSTRs in series. Here $N$ is reasonably larger than 1. In practice, a series of 50 or more tanks usually gives an RTD sufficiently close to that of a PFR.

**Selective Acetylene Hydrogenation Reactions (Mostoufi et al. 2005)**

There are 3 major gas-phase reactions in this system (Bos et al. 1993, Westerterp et al. 2002):

\[
\begin{align*}
C_2H_2 + H_2 & \rightarrow C_2H_4 \quad (3) \\
C_2H_4 + H_2 & \rightarrow C_2H_6 \quad (4) \\
C_2H_2 + 2H_2 & \rightarrow C_2H_6 \quad (5)
\end{align*}
\]

Here we denote species $i = 1$ for $C_2H_2$; $i = 2$ for $H_2$; $i = 3$ for $C_2H_4$; and $i = 4$ for $C_2H_6$. Since kinetic rate of reaction (5) is much slower than (3) and (4), it can be

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**Fig. 1:** Tubular fixed-bed catalytic reactor represented by a series of $N$ CSTRs.
disregarded here. The molecular weight of species \(i\) is: \(M_1 = 26\) (acetylene), \(M_2 = 2\) (hydrogen), \(M_3 = 28\) (ethylene), \(M_4 = 30\) (ethane).

Figure 1 illustrates the schematic diagram of a 1-D tubular fixed-bed reactor vessel with axial dispersion, as represented by a series of \(N\) CSTRs of equal volumes. 

\[
V_j = \frac{V_{\text{tot}}}{N} = \Delta V = A \Delta z \tag{6}
\]

The mass balance equation for species \(i\) \((i = 1, 2, 3, 4)\) in compartment \(j\) \((j = 1, 2, ..., N)\) is given by

\[
\frac{dC_{ij}}{dt} = \frac{1}{\varepsilon \Delta V} (F_{ij-1} - F_{ij}) + \frac{\rho C}{\varepsilon} r_{ij} = \frac{1}{\varepsilon \Delta V} (Q_j - C_{ij-1} - Q_j C_{ij}) + \frac{\rho C}{\varepsilon} r_{ij} \tag{7}
\]

The volumetric flow rate \(Q_j\) generally depends on the molar composition, pressure and temperature of the fluid stream. Strictly speaking, \(Q_j\) should be determined by solving the equation of motion. As a simplification, we assume here that there is no accumulation of total mass in any compartment \(j\), even though there might be accumulation or depletion of moles of species \(i\) \((i = 1, 2, 3, 4)\) in it. Therefore, for \(j = 1, 2, ..., N:\)

\[
Q_{j-1} C_{Tj-1} M_{\text{avg} j-1} = Q_j C_{Tj} M_{\text{avg} j} \tag{8}
\]

Here \(M_{\text{avg} j}\) is the average molecular weight of the fluid mixture in compartment \(j\).

\[
F_{Tj} = \sum_{i=1}^{4} F_{ij} = Q_j C_{Tj} \tag{9}
\]

\[
C_{Tj} = \sum_{i=1}^{4} C_{ij} \tag{10}
\]

The reaction rate \(r_i\) is based on the kinetics obtained experimentally by Mostoufi et al. (2005) using a commercial catalyst Pd/Al2O3 (G58-B made by Sud-Chemie), as follows: 

Rate of hydrogenation of acetylene \(C_2H_2\) \((i = 1\) via (3)) \([\text{kmol/kg-cat}\cdot\text{s}]\) is

\[
-r_1 = \frac{k_1 P_1 P_2}{[1 + K_1 P_3][1 + K_2 P_2]} \tag{11}
\]

\[
k_1 = 48.01 \exp(-146.8/T) \tag{12}
\]

\[
K_1 = 584.59 \exp(668.6/T) \tag{13}
\]

\[
K_2 = 2.855 \exp(404.3/T) \tag{14}
\]

Rate of ethane production \((i = 4\) via (4)) by hydrogenation of ethylene \(C_2H_4\) is

\[
r_4 = \frac{k_2 P_3 P_2}{[1 + K_3 P_3][1 + K_2' P_2]} \tag{15}
\]

\[
k_2 = 202.67 \exp(-4784/T) \tag{16}
\]

\[
K_3 = 0.0742 \exp(1502.7/T) \tag{17}
\]

\[
K_2' = 2.89 \exp(400/T) \tag{18}
\]

Rate of generation of hydrogen \((i = 2)\) is

\[
r_2 = -r_4 + r_1 \tag{19}
\]

Rate of generation of ethylene \((i = 3)\) is

\[
r_3 = -r_1 - r_4 \tag{20}
\]

A second subscript \(j\) is added to eqns. (11) – (20) to specifically denote the condition in compartment \(j\). Total pressure in compartment \(j\) \((P_j)\) is given by
\[ P_{Tj} = \sum_{i=1}^{4} P_{ij} = \sum_{i=1}^{4} C_{ij} P_{j} / C_{Tj} \]
\[ = \sum x_{ij} P_{j} \]  

(21)

From ideal gas law,
\[ P_{ij} = \frac{n_{ij} R T_{j}}{\Delta V} = C_{ij} R T_{j} \]  

(22)

The corresponding inlet and initial conditions are as follows:
Inlet of plug-flow reactor: \( F_{T0} = Q_{0} c_{T0} \) is given
At \( t = 0 \), \( c_{ij} \) are given (\( i = 1, 2, 3, 4; j = 1, 2, \ldots, N \))
\( F_{t0} = Q_{0} c_{t0} \) are given (\( i = 1, 2, 3, 4 \))

(23)
(24)
(25)

Similarly, the thermal energy balance equation for the adiabatic reactor can be derived and summarized as follows. Note that axial and radial heat conduction may be ignored in this case.

\[ \frac{dT_{j}}{dt} = \frac{1}{\varepsilon H_{j}} \left\{ \frac{1}{\Delta V} \left[ H_{j-1} Q_{j-1} T_{j-1} - H_{j} Q_{j} T_{j} \right] + \rho_{c} \left[ \Delta H_{R1} r_{3j} - \Delta H_{R2} r_{4j} \right] \right\} - \frac{T_{j} dH_{j}}{H_{j} dt} \]

(26)

For convenience sake, \( H_{j} \) and its time derivative are defined as
\[ H_{j} = \sum_{i=1}^{4} C_{ij} c_{pi} + \rho_{c} c_{pcat} \]  

(27)

\[ \frac{dH_{j}}{dt} = \sum_{i=1}^{4} c_{pi} \frac{dC_{ij}}{dt} \]  

(28)

The reactor inlet and initial conditions are given by
Inlet of reactor: \( T_{0i}, P_{T0}, C_{io}, Q_{o} \) or \( F_{To} \) (\( i = 1, 2, 3, 4 \))
At \( t = 0 \), \( T_{j}, H_{j} \) are given (\( j = 1, 2, \ldots, N \))

(29)
(30)

**SIMULATION METHOD & CONDITIONS**

Together with the relevant algebraic equations, the above set of non-linear first-order ODEs [equations (7), (26) and (28)] can be integrated numerically using 4th-order Runge-Kutta algorithm and Excel VBA (Visual BASIC in Applications). As a first step, only the first bed of a multi-bed reactor will be investigated. Table 1 shows the input and parametric values used in the present investigation.

Note that the average MW of the feedstock is 27.9 kg/kmol, and the feed rate (base case) is 30.56 kg/s (1.0962 kmol/s; 0.78210 m³/s).

Property of catalyst: G58C, Pd-Ag/Al₂O₃
Pellet size: 4.0 mm and 3.0 mm (equivalent diameter) for OPX and OPY, respectively
Coating depth (shell thickness) of active
phase: 0.2 mm.
Catalyst pellet density: 1400 kg/m$^3$;
specific surface area: $\sim$30 m$^2$/g
True density of Al$_2$O$_3$ (support): 3690 kg/m$^3$
Pellet porosity = 62%

**SIMULATION RESULTS AND DISCUSSION**

Three independent simulation cases are investigated and discussed here.

Figure 2 shows the transient axial temperature profiles along the normalized reactor length for the base case. Before steady state (SS) is reached, there is an overshoot of the reactor outlet temperature at time $t = 5$s. Figure 3 shows the effect of inlet temperature $T_{in}$ on the temperature profiles at $t = 1$s and 10$s$. Though omitted here, the magnitude of the overshoot is found to increase as $T_{in}$ increases. In fact, if $T_{in}$ is too high, the overshoot peak may increase exponentially to cause reaction runaway.

Figures 4 and 5 show the effect of $T_{in}$ on the axial concentration profiles of C$_2$H$_2$ and C$_2$H$_4$, respectively. As expected, conversion of C$_2$H$_2$ is faster when $T_{in}$ is

<table>
<thead>
<tr>
<th>Variables/Parameters</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene (C$_2$H$_2$)</td>
<td>%</td>
<td>1.5</td>
</tr>
<tr>
<td>Ethylene (C$_2$H$_4$)</td>
<td>%</td>
<td>83.6</td>
</tr>
<tr>
<td>Ethane (C$_2$H$_6$)</td>
<td>%</td>
<td>13.3</td>
</tr>
<tr>
<td>Hydrogen (H$_2$)</td>
<td>%</td>
<td>1.6</td>
</tr>
<tr>
<td>Influent stream</td>
<td>kmol/s</td>
<td>1.0962 (base)</td>
</tr>
<tr>
<td>Reactor length (OPX: base)</td>
<td>m</td>
<td>OPX 2.73; OPY 3.35</td>
</tr>
<tr>
<td>Reactor diameter (OPX: base)</td>
<td>m</td>
<td>OPX 2.8; OPY 3.35</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>K</td>
<td>298 (base) 303,308,313</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>barA</td>
<td>21</td>
</tr>
<tr>
<td>Packing density of catalyst</td>
<td>kg/m$^3$</td>
<td>720</td>
</tr>
<tr>
<td>Bed voidage ($\varepsilon$)</td>
<td>m$^3$/m$^3$</td>
<td>0.49</td>
</tr>
<tr>
<td>Compartment number ($N$)</td>
<td></td>
<td>50 (base), 20, 10</td>
</tr>
</tbody>
</table>

**Fig. 2:** Temperature profile (base case)
higher, and this difference is more pronounced at $t = 1\text{s}$. Since the gas mixture volume expands when $T_{in}$ is higher, the inlet concentration of $C_2H_4$ becomes lower, though the inlet composition and total flow rate remain constant. Nevertheless, its concentration profile at $t = 1\text{s}$ is somewhat closer to the steady state when $T_{in}$ is higher.

**Simulation Case 2: Effect of number of tank compartments ($N$) (axial dispersion effect)**

Figures 6 and 7 show the effect of axial dispersion on the temperature and $C_2H_2$ concentration profiles, respectively. The dispersion level increases monotonically as the total number of compartments $N$ decreases from 50 (essentially plug flow).
to 20 and 10. As expected, the profiles develop faster when the dispersion level increases, and this effect still slightly remains after SS is reached. The conversion of \( \text{C}_2\text{H}_2 \) at reactor outlet is slightly reduced by axial dispersion effect.

**Fig. 5:** Effect of \( T_{in} \) on \( \text{C}_2\text{H}_4 \) conc. profile

**Fig. 6:** Effect of \( N \) on temp. profile

**Fig. 7:** Effect of \( N \) on \( \text{C}_2\text{H}_2 \) conc. profile
Simulation Case 3: Effect of influent flow rate on OPX and OPY reactors having different reactor configurations

Here -20% and +20% deviations in the total flow rate (flow ratio $F_R = 0.8$ and 1.2, respectively) on the behavior of two commercial reactors of different sizes in olefins plants, code-named OPX and OPY, are investigated. As shown in Table 1, the reactors have different diameters and lengths, though they are operated under similar condition. Figures 8 - 11 show that the SS temperature and $C_2H_2$ concentration profiles inside both reactors take somewhat a longer axial distance to become fully developed when total flow rate or $F_R$ increases because of the resulting shorter residence time. As a result, Figures 12 and 13 reveal that the total conversions of $C_2H_2$ and $H_2$ for the smaller OPX reactor become less than those of the larger OPY reactor, though OPX shows a higher selectivity of $C_2H_2$ conversion to $C_2H_4$ than OPY. Comparison between Figures 8 and 9 reveals that the OPY reactor not only has a higher average...
temperature but its temperature also rises faster than OPX. This could be a root cause of the significantly faster catalyst deactivation rate observed in OPY.

CONCLUSIONS

Though fast and efficient to compute, the present model still has room for improvement. The simulation results agree qualitatively with the plant data but not sufficiently quantitatively due to 2 reasons. First, the kinetic expressions given by Mostoufi et al. (2005) do not consider the presence of Ag promoter, or the role of CO in enhancing the acetylene hydrogenation selectivity, which existed in the said olefins

![Fig. 10: Effect of FR on OPX C2H2 conc. profile](image1)

![Fig. 11: Effect of FR on OPY C2H2 conc. profile](image2)
plants. Second, the use of RTD equivalent to a series of fully mixed compartments to take acc
account of the axial dispersion in plug flow is theoretically proven to be exactly correct only in the case of isothermal first-order reaction system. Its application to a nonisothermal, nonlinear set of two parallel reactions can, therefore, be expected to give only approximate results. The authors will work to refine the kinetic rate expressions for Pd-Ag/Al₂O₃ catalyst and improve our next predictions against plant data.

NOMENCLATURE

\( C_i \) : Concentration of species \( i \) [kmol/m³-fluid]

\( C_{ij} \) : Concentration of species \( i \) in reactor compartment \( j \) [kmol/m³-fluid]
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{ij}$</td>
<td>Total molar concentration in compartment $j$ [kmol/m$^3$-fluid]</td>
</tr>
<tr>
<td>$c_{pi}$</td>
<td>Specific heat of species $i$ [kJ/kmol·K] (assumed independent of pressure)</td>
</tr>
<tr>
<td>$c_{pcat}$</td>
<td>Specific heat of catalyst [kJ/kg-cat·K] (assumed to be constant)</td>
</tr>
<tr>
<td>$F_{ij}$</td>
<td>Molar flow rate of species $i$ [kmol/s] out of compartment $j$ (and into $j + 1$)</td>
</tr>
<tr>
<td>$F_{Tj}$</td>
<td>Total molar flow from compartment $j$ [kmol/s]</td>
</tr>
<tr>
<td>$H_j$</td>
<td>$\sum_{i=1}^{k} C_{ij} c_{pi} + \rho_c c_{pcat}/\varepsilon$</td>
</tr>
<tr>
<td>$\Delta H_a$</td>
<td>Adsorption activation energy difference $= E_{\text{adsorption}} - E_{\text{desorption}}$ [kJ/mol]</td>
</tr>
<tr>
<td>$\Delta H_{Rk}$</td>
<td>Heat of reaction of reaction no. $k$ [kJ/kmol] ($k = 1$ for hydrogenation of acetylene; $k = 2$ for hydrogenation of ethylene) $\Delta H_{R1}^{-} @ 298 \text{ K} = -172,000$ kJ/kmol; $\Delta H_{R2}^{-} @ 298 \text{ K} = -137,000$ kJ/kmol</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Adsorption equilibrium constant for species $i$ [bar$^{-1}$]</td>
</tr>
<tr>
<td>$k_k$</td>
<td>Reaction rate constant of reaction $k$ ($k = 1, 2$) [kmol/s·bar$^2$]</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Partial pressure (absolute) of species $i$ [bar]</td>
</tr>
<tr>
<td>$P_{ij}$</td>
<td>Partial pressure (absolute) of species $i$ in reactor compartment $j$ [bar]</td>
</tr>
<tr>
<td>$P_{Tj}$</td>
<td>Total pressure in compartment $j$ [bar]</td>
</tr>
<tr>
<td>$Q_j$</td>
<td>Volumetric flow rate from compartment $j$ [m$^3$/s]</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Gas constant $= 8.314$ [kJ/kmol·K] $= 0.08314$ [m$^3$·bar/kmol·K]</td>
</tr>
<tr>
<td>$r_{ij}$</td>
<td>Rate of generation by reactions of species $i$ in compartment $j$ [kmol/kg-cat·s]</td>
</tr>
<tr>
<td>$r_i$</td>
<td>Rate of generation of species $i$ [kmol/kg-cat·s]</td>
</tr>
<tr>
<td>$T_j$</td>
<td>Temperature of fluid in reactor compartment $j$ [K]</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>Length of each tank compartment [m]</td>
</tr>
<tr>
<td>$x_{ij}$</td>
<td>Mole fraction of species $i$ in compartment $j$ [-]</td>
</tr>
<tr>
<td>$t$</td>
<td>Time [s]</td>
</tr>
<tr>
<td>$V_j$</td>
<td>Volume of reactor compartment $j$ [m$^3$] $= \frac{V_{TOT} N}{N}$</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Packed density of catalyst [kg-cat/m$^3$-bed]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Bed voidage [-] or [m$^3$-void/m$^3$-bed]</td>
</tr>
<tr>
<td>$\Delta V$</td>
<td>Change in reactor volume $= \frac{\Delta V}{N}$</td>
</tr>
</tbody>
</table>

Greek letter

- $\varepsilon$: Bed voidage [-] or [m$^3$-void/m$^3$-bed]

Subscripts

- $o$: Inlet of reactor ($C_{ij0}, C_{io}, C_{To}, F_{io}, P_{To}, Q_{o}, T_{o}, T_{j0}$)

REFERENCES


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